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Structural Effects on the pH-dependent Fluorescence of Naphthalenic Derivatives and Consequences for Sensing/Switching

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Dedicated to Jean-Pierre Desvergne and to Hubert Le Bozec

Abstract

Naphthalenic compounds are a rich resource for designers of fluorescent sensing/switching/logic systems. The degree of ICT character in the fluorophore excited states can vary from negligible to substantial. Naphthalene-1,8;4,5-diimides (**11-13**), 1,8-naphthalimides (**16**) and 4-chloro-1,8-naphthalimides (**15**) are of the former type. The latter type is represented by the 4-alkylamino-1,8-naphthalimides (**1**). Whether ICT-based or not, these serve as the fluorophore in 'fluorophore-spacer-receptor' switching systems where PET holds sway until the receptor is bound to H⁺. On the other hand, 4-dialkylamino-1,8-naphthalimides (**3-4**) show modest H⁺-induced fluorescence switching unless the 4-dialkylamino group is a part of a small ring (**5**). Electrostatic destabilization of a non-emissive twisted ICT excited state is the origin of this behaviour. An evolution to the non-emissive twisted ICT excited state is responsible for the weak emission of the model compound **6** (and related structures **7** and **8**) across the pH range. Twisted ICT excited states are also implicated in the switch **9** and its model compound **10**, which are based on the 6-dialkylamino-3H-benzimidazo[2,1-a]benz[d,e]isoquinolin-3-one fluorophore.

Introduction

Naphthalimides and related compounds¹ have found much use in the fluorescent sensing/switching sphere.²⁻²⁵ Some have featured as molecular logic gates.²⁶⁻³⁷ Others have even found commercial success in blood electrolyte diagnostics.³⁸⁻⁴¹ Beside convenient synthetic routes, these compounds have very useful optical and redox properties which lead to the above applications. Compound **1**² is a well-behaved fluorescent PET (photoinduced electron transfer) system⁴²⁻⁴⁵ of the 'fluorophore-spacer-receptor' format,^{46,47} whose fluorescence responds sharply to H⁺. Briefly, the diethylamino receptor launches an electron to the photoexcited fluorophore so that fluorescence is quenched. Upon binding H⁺ to the diethylamino receptor, this PET pathway is arrested so that fluorescence emerges. The photogenerated electric field of the ICT (internal charge transfer) excited state of the aminonaphthalimide fluorophore contributes to the PET efficiency.² This leads conceptually to the mimicry of the path-selective PET in the bacterial photosynthetic reaction centre^{6,25} and to the development of fluorescent PET systems for neural signalling.⁴⁸ Now we examine several structural variations on **1**, some of which have major influences on pH-dependent fluorescence behaviour.

Experimental

Materials

N-Butyl-4-chloro-1,8-naphthalimide (**2**)

4-Chloro-1,8-naphthalic anhydride (2.9 g, 12.5 mmol), *n*-butylamine (0.9 g, 12.5 mmol) and toluene (30 ml) were refluxed for 4 hr. The solvent was distilled off under vacuum. Crystallization from acetic acid gave pale yellow crystals. Yield 60%, m.p. 180-181 C. Found: $M^+ = 287.0801$. $C_{16}H_{14}NO_2Cl$ requires 287.0713; $\delta_H(CDCl_3)$ 7.96-8.59 (m, 5H, ArH), 4.05 (t, 2H, NCH_2), 1.57 (m, 2H, NCH_2CH_2), 1.30 (m, 2H, $MeCH_2$), 0.89 (t, 3H, CH_3).

N-Butyl-4-[*N'*-methyl-2'-(*N''*,*N''*-diethylamino)ethyl]amino-1,8-naphthalimide (**3**)

Compound **2** (1.0 g, 3.5 mmol) was dissolved in *N,N*-diethyl-*N'*-methylethylenediamine (4.5 g, 35 mmol) and heated at 100 C for 4 hr. The mixture was evaporated to dryness under vacuum. Crystallization from diethylether/hexane gave yellow plates. Yield 68%, m.p. 147-149 C. Found: $M+H^+ = 382.2495$. $C_{23}H_{32}N_3O_2$ requires 382.2495; $\delta_H(CDCl_3)$ 7.33-8.62 (m, 5H, ArH), 4.17 (t, 2H, $OCNCH_2$), 3.93 (t, 2H, $ArNCH_2$), 3.17-3.23 (brm, 6H, $MeCH_2N$ and Et_2NCH_2), 3.12 (s, 3H, NCH_3), 1.72 (m, 2H, $OCNCH_2CH_2$), 1.44 (m, 2H, $MeCH_2$), 1.09 (t, 6H, NCH_2CH_3), 0.97 (t, 3H, CH_2CH_3).

N-Butyl-4-[*N'*-methyl-2'-(*N''*,*N''*-dimethylamino)ethyl]amino-1,8-naphthalimide (**4**)

Compound **4** was prepared according to a procedure analogous to that used for **3**, except that *N,N*-diethyl-*N'*-methylethylenediamine was replaced with *N,N,N'*-trimethylethylenediamine. Crystallization from diethylether/hexane gave orange crystals. Yield 62%, m.p. 138-139 C. Found: $M+H^+ = 354.2062$. $C_{21}H_{28}N_3O_2$ requires 354.2181; $\delta_H(CDCl_3)$ 7.27-8.59 (m, 5H, ArH), 4.17 (t, 2H, $OCNCH_2$), 3.97 (t, 2H, $ArNCH_2$), 3.22 (s, 6H, $N(CH_3)_2$), 3.19 (t, 2H, Me_2NCH_2), 3.14 (s, 3H, NCH_3), 1.70 (m, 2H, $OCNCH_2CH_2$), 1.44 (m, 2H, $MeCH_2$), 1.01 (t, 6H, NCH_2CH_3), 0.97 (t, 3H, CH_2CH_3).

N-Butyl-4-*N'*-methylpiperazino-1,8-naphthalimide (**5**)

Compound **5** was prepared according to a procedure analogous to that used for **3**, except that *N,N*-diethyl-*N'*-methylethylenediamine was replaced with *N*-methylpiperazine. Crystallization from ethanol gave bright orange crystals. Yield 11%, m.p. 118-119 C. Found: C, 71.5; H, 6.9; N, 11.7. $C_{21}H_{25}N_3O_2$ requires C, 71.8; H, 7.2; N, 11.9%; $\delta_H(CDCl_3)$ 7.24-8.59 (m, 5H, ArH), 4.17 (t, 2H, $OCNCH_2$), 3.30 (t, 4H, $ArNCH_2$), 2.74 (t, 4H, $MeNCH_2$), 2.47 (s, 3H, NCH_3), 1.70 (m, 2H, $OCNCH_2CH_2$), 1.43 (m, 2H, $MeCH_2$), 0.98 (t, 3H, CH_2CH_3); m/z (%) 351 (M^+).

N-Butyl-4-morpholino-1,8-naphthalimide (**6**)

Compound **6** was prepared according to a procedure analogous to that used for **5**, except that *N*-methylpiperazine was replaced with morpholine. Crystallization from ethanol gave yellow crystals. Yield 36%, m.p. 124-125 C. Found: C, 71.1; H, 6.5; N, 8.3. $C_{20}H_{22}N_2O_3$ requires C, 71.0; H, 6.6; N, 8.3%; $\delta_H(CDCl_3)$ 8.61-7.24 (m, 5H, ArH), 4.17 (t, 2H, $OCNCH_2$), 4.02 (t, 4H, $ArNCH_2$), 3.26 (t, 4H, OCH_2), 1.70 (m, 2H, $OCNCH_2CH_2$), 1.43 (m, 2H, $MeCH_2$), 0.98 (t, 3H, CH_3); m/z (%) 338 (M^+).

N-2'-(*N'*,*N'*-diethylamino)ethyl-4-morpholino-1,8-naphthalimide (**7**)

Compound **7** was prepared according to a procedure analogous to that used for **6**, except that **2** was replaced with *N*-2'-(diethylamino)ethyl-4-chloro-1,8-naphthalimide.⁵ Crystallization from diethylether/methanol gave yellow-orange

crystals. Yield 26%, m.p. 123-124 C. Found: C, 69.1; H, 7.3; N, 11.0. $C_{22}H_{27}N_3O_3$ requires C, 69.3; H, 7.1; N, 11.0%; $\delta_H(CDCl_3)$ 7.25-8.57 (m, 5H, ArH), 4.28 (t, 2H, $OCNCH_2$), 4.02 (t, 4H, OCH_2), 3.26 (t, 4H, $ArNCH_2$), 2.80 (t, 2H, $OCNCH_2CH_2$), 2.63 (q, 4H, $MeCH_2$), 1.09 (t, 6H, CH_3); m/z (%) 381 (M^+).

N-2'-(morpholino)ethyl-4-morpholino-1,8-naphthalimide (**8**)

Compound **8** was prepared according to a procedure analogous to that used for **6**, except that **2** was replaced with *N*-2'-(morpholino)ethyl-4-chloro-1,8-naphthalimide.⁵ Crystallization from chlorobenzene gave bright yellow crystals. Yield 33%, m.p. 196-197 C. Found: C, 66.8; H, 6.2; N, 10.3. $C_{22}H_{25}N_3O_4$ requires C, 66.8; H, 6.4; N, 10.6%; $\delta_H(CDCl_3)$ 7.26-8.59 (m, 5H, ArH), 4.35 (t, 2H, $OCNCH_2$), 4.02 (t, 4H, $ArNCH_2CH_2$), 3.65 (t, 4H, $CH_2NCH_2CH_2O$), 3.24 (t, 4H, $ArNCH_2$), 2.72 (t, 2H, $OCNCH_2CH_2$), 2.57 (t, 4H, $CH_2NCH_2CH_2O$); m/z (%) 395 (M^+).

6-*N'*-Methylpiperazino-3*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-3-one (**9**)

6-Chloro-3*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-3-one (3.2 g, 0.01 mol),^{49,50} *N*-methylpiperazine (9 ml, 0.08 mol), hydrated $CuSO_4$ (0.4 g, 1.6 mmol) and 2-methoxyethanol (100 ml) were refluxed for 6 hr. The reaction mixture was poured into water to give the crude product. This was dissolved in HCl (0.1 M), washed with CH_2Cl_2 , basified with NaOH and extracted into CH_2Cl_2 and the solvent evaporated off. Crystallization from CH_2Cl_2 gave bright orange crystals. Yield 20%, m.p. 235-236 C. Found: C, 74.7; H, 5.3; N, 14.9. $C_{23}H_{20}N_4O$ requires C, 75.0; H, 5.5; N, 15.3%; $\delta_H(CDCl_3)$ 7.22-8.78 (m, 9H, ArH), 3.35 (t, 4H, $ArNCH_2$), 2.65 (t, 4H, $MeNCH_2$), 2.46 (s, 3H, NCH_3); m/z (%) 368 (M^+).

6-Morpholino-3*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-3-one (**10**)

Compound **10** was prepared according to a procedure analogous to that used for **9**, except that *N*-methylpiperazine was replaced with morpholine. Also, the acidification/basification routine was not used. Crystallization from chlorobenzene gave bright orange crystals. Yield 44%, m.p. 228-232 C. Found: $M^+ = 355.1319$. $C_{22}H_{17}N_3O_2$ requires 355.1319; $\delta_H(CDCl_3)$ 7.24-8.78 (m, 9H, ArH), 4.01 (t, 4H, OCH_2), 3.22 (t, 4H, NCH_2).

N,N'-bis[(2'-(*N''*,*N'''*-dimethylamino)ethyl)-1,8;4,5-naphthalenediimide (**11**)

1,8;4,5-Naphthalenetetracarboxylic dianhydride (3.4 g, 12.5 mmol), *N,N*-dimethylethylenediamine (2.2 g, 25 mmol) and toluene (50 ml) was refluxed for 4 hr. The mixture was evaporated to dryness under vacuum and washed with acetone to give an orange solid. Yield 65%, m.p. 272-274 C (lit.⁵¹ m.p. 279-281). Found: C, 64.1; H, 5.7; N, 13.5. $C_{22}H_{24}N_4O_4$ requires C, 64.7; H, 5.9; N, 13.7%; $\delta_H(CDCl_3)$ 8.74 (s, 4H, ArH), 4.34 (t, 4H, $OCNCH_2$), 2.67 (t, 4H, Me_2NCH_2), 2.34 (s, 12H, NCH_3); m/z 408 (M^+).

N,N'-bis[(2'-(morpholino)ethyl)-1,8;4,5-naphthalenediimide (**12**)

Compound **12** was prepared according to a procedure analogous to that used for **11**, except that *N,N*-dimethylethylenediamine was replaced with 4-(2'-amino)ethylmorpholine. Orange solid. Yield 65%, m.p. 220-221 C. Found: $M^+ = 492.2024$. $C_{26}H_{28}N_4O_6$ requires 492.2009; $\delta_H(CDCl_3)$ 8.77 (s, 4H, ArH), 4.37 (t, 4H, $OCNCH_2$), 3.65 (t, 8H, NCH_2CH_2O), 2.71 (s, 4H, $OCNCH_2CH_2$), 2.58 (bm, 8H, NCH_2CH_2O).

N,N'-bis[(3'-(*N,N'*-dimethylamino)propyl]-1,8;4,5-naphthalenediimide (**13**)

Compound **13** was prepared according to a procedure analogous to that used for **11**, except that *N,N*-dimethylethylenediamine was replaced with *N,N*-dimethylpropylenediamine. Orange solid. Yield 63%, m.p. 263-264 °C. Found: C, 61.3; H, 5.9; N, 11.9. $C_{24}H_{28}N_4O_4$ requires C, 61.0; H, 5.9; N, 11.9%; $\delta_H(CDCl_3)$ 8.74 (s, 4H, ArH), 4.26 (t, 4H, OCNCH₂), 2.44 (t, 4H, Me₂NCH₂), 2.34 (s, 12H, NCH₃), 1.92 (q, 4H, OCNCH₂CH₂); m/z 436 (M^+).

Equipment and methods

UV–Visible absorption and fluorescence emission spectra were recorded on Perkin-Elmer Lambda 9 and Perkin-Elmer LS-55/LS5B spectrometers, respectively. Nuclear magnetic resonance spectra were obtained with a Bruker AC250 spectrometer. Mass spectra were obtained with a VG MS902 instrument. pH measurements employed a Jenway 3310 pH meter with a glass electrode.

Results and discussion

The important parameters which characterize the H^+ -induced fluorescence switching action of **1** have been published² and are summarized in Table 1. Compound **1** is strongly emissive in acid media ($\phi_{Flu.acid} = 0.76$) but is quenched by a factor of 25 in base. Notably, acid media induce a 18 nm blue-shift in the absorption spectrum due to destabilization of the Franck-Condon ICT excited state by the neighbouring protonated amine receptor. A similar effect is discernible regarding the thermally equilibrated ICT excited state in the fluorescence emission spectra.

Table 1. Various parameters for **1-10** (except **2**) determined via pH-dependent uv-visible absorption and fluorescence spectroscopy.^a

Parameter	1	3	4	5	6	7	8	9	10
$\lambda_{Abs.acid}$	431	399	398	387	402	403	404	411	416
$\log \epsilon_{acid}^b$	4.22	4.14	4.32	4.14	4.01	4.07	4.04	4.30	4.03
$\lambda_{Abs.base}$	449	439	439	405	402	402	402	427	416
$\log \epsilon_{base}^b$	4.22	4.14	4.32	4.08	4.01	4.04	4.04	4.30	4.03
$\lambda_{Isosbestic}$	440	414	416	404	- ^h	- ^h	- ^h	416	- ^h
pK_a^c	8.4	8.9	8.3	7.4	- ^h	- ^h	- ^h	7.3	- ^h
$\lambda_{Flu.acid}$	538	531	528	520	538	540 ^j	540 ^l	500	545
$\phi_{Flu.acid}^d$	0.76	0.031	0.033	0.58	0.006	0.004	0.006	0.55	0.044
$\lambda_{Flu.base}$	549	530	527	- ^g	538	540 ^j	540 ^l	- ^g	545
$\phi_{Flu.base}^d$	0.030	0.011	0.010	0.001	0.006	0.005	0.007	0.003	0.042
FE^e	25	2.8	3.3	480	1.1	0.9 ^k	0.9 ^m	200	1.0
pK_a^f	8.7	8.7	8.1	7.2	- ⁱ	8.5	6.0	7.3	- ⁱ

a. $10^{-5}M$ in methanol:water (1:4, v/v). Fluorescence emission spectra are obtained by excitation at $\lambda_{Isosbestic}$. The subscripts 'acid' and 'base' in some of the parameters refer to the limiting value of a given parameter when the acid or base condition is increased respectively. Data for compound **1** is from ref. 2.

b. ϵ in $M^{-1}cm^{-1}$.

c. obtained by analyzing the pH dependence of the Absorbance (A) at a given wavelength according to the equation $\log[(A_{acid} - A)/(A - A_{base})] = pH - pK_a$.^{52,53} Uncertainty = 0.1.

d. uncertainty = 0.001 or 10% whichever is the larger.

e. H^+ -induced fluorescence enhancement factor = $\phi_{Flu.acid}/\phi_{Flu.base}$.

- f. obtained by analyzing the pH dependence of the fluorescence intensity (I_{Flu}) or fluorescence quantum yield (ϕ_{Flu}) at a given wavelength according to the equation $\log[(\phi_{\text{Flu,acid}} - \phi_{\text{Flu}})/(\phi_{\text{Flu}} - \phi_{\text{Flu,base}})] = \text{pH} - \text{pK}_{\text{a}}'$.⁵⁴ Uncertainty = 0.1.
- g. indeterminable owing to the low value of $\phi_{\text{Flu,base}}$.
- h. indeterminable owing to the lack of an analyzable dependence of absorbance on pH.
- i. indeterminable owing to the lack of an analyzable dependence of fluorescence on pH.
- j. shoulder at 476 nm.
- k. $(I_{\text{Flu,acid}}/I_{\text{Flu,base}})_{476 \text{ nm}} = 2.1$.
- l. shoulder at 481 nm.
- m. $(I_{\text{Flu,acid}}/I_{\text{Flu,base}})_{476 \text{ nm}} = 2.0$.

Replacing the hydrogen at the 4-amino group of **1** by a methyl gives compound **3**. While **3** contains a diethylamino receptor, its sibling **4** carries a dimethylamino receptor instead. The H^+ -induced absorption spectral blue-shifts seen for **3** (40 nm) and **4** (41 nm) are similar to those of **1**, though noticeably larger (Table 1). The fluorescence emission spectra of **4** (Figure 1) display a H^+ -induced fluorescence enhancement factor (FE) of just 3.3. Even more crucially, the fluorescence quantum yield in acid is only 0.033. Thus, protonation does not kill off the major channel(s) of excited state deactivation. H^+ -induced PET suppression plays a minor role, if at all.

Converting the 4-monoalkylamino group of **1** into the 4-dialkylamino group of **3** and **4** causes steric hindrance with the peri-hydrogen at the 5-position unless relieved by twisting about the aromatic C-N bond. Such twisting, and the resulting reduction of π -conjugation, is mirrored in lower absorption spectral wavelengths ($\lambda_{\text{Abs,base}} = 439 \text{ nm}$ for **3** and **4** c.f. 449 nm for **1**). Lower ICT-type emission spectral wavelengths (Table 1) also support this conclusion. An extreme case of twisting about naphthalenic C-N bonds due to steric hindrance is seen in the proton sponge behaviour of 1,2-bis(dimethylamino)naphthalene.⁵⁵

ICT excited states which can twist about aromatic C-N bonds lead to TICT (twisted intramolecular charge transfer) excited states.⁵⁶⁻⁵⁸ Though emissive cases are in the minority, these states lead to deexcitation pathways in many flexible fluorophores.^{57,58} Such twisted ICT excited states undergo deconjugation between electron-donor and -acceptor segments so that full charge separation occurs, with suitable stabilization by polar solvents. The thermodynamics of such processes are very similar to those seen in PET systems.⁵⁶⁻⁵⁹ Pre-twisting in the ground state leads to an extra propensity for twisted ICT excited state formation.^{57,58} This situation applies to observations regarding compounds **3** and **4** in their basic form, with the dialkylamino unit and the naphthalimide moiety serving as the donor and acceptor of the twisted ICT state respectively. An approximate valence bond representation is shown in structure **14**. A characteristic emission would be good evidence of twisted ICT states but this has been seen in only a small minority of these cases.⁵⁶⁻⁵⁸ So it is not surprising that we failed to see any such evidence with our basic spectrometers.

When the diethyl- or dimethyl-aminoethyl side-chains are protonated, the new cationic charge is positioned two methylene groups away from the radical cation centre of the twisted ICT excited state. Naturally, this electrostatic destabilization of the twisted ICT state reduces the efficiency of this deexcitation channel. Hence, the H^+ -induced FE value of 3.3 which is seen for **4** (Figure 1), for instance, is understandable.

Case **5**, incorporating a piperazine ring into the dialkylamino donor portion of the twisted ICT state, takes the effect to an extreme. When compared to **3**, compound **5** suffers an even lower value of $\lambda_{\text{Abs,base}}$ (405 nm for **5** c.f. 439 nm for **3**). Thus the pre-twisting in the ground state is greater for **5**, due to reduced flexibility of the piperazine ring c.f. the alkyl chain in **3**. So it is not surprising that the twisted ICT process is the strongest and the fluorescence of **5** is the weakest ($\phi_{\text{Flu,base}} = 0.001$) seen in this work. However, protonation of **5** gives a dramatic fluorescence enhancement ($\text{FE} = 480$) and the $\phi_{\text{Flu,acid}}$ value of 0.58 is the highest observed in the present experimental work. Even though the new cationic charge is still positioned two methylene groups away from the radical cation centre of the twisted ICT state, the piperazine ring forces the separation distance to be smaller. Therefore the electrostatic destabilization of the twisted ICT state is stronger. In this situation, the N-C-C-N atom set involves a gauche arrangement of the two C-N bonds. In contrast, protonated and excited **3** involves an antiperiplanar arrangement which reduces the electrostatic repulsion as far as possible. It is worth noting that, from an operational viewpoint, compound **5** behaves like a classical fluorescent PET sensor⁶⁰ for H^+ even though a careful structure-activity analysis reveals a twisted ICT state at work. During their extensive studies, Tian et al examined a structure which is **5** but with a methyl instead of the n-butyl group at the imide position and attributed a PET mechanism to it.⁶¹ Other cases in the literature which may have been assigned too hurriedly as fluorescent PET sensors can be investigated in this way.

When the N-methylpiperazine ring in **5** is mutated to a morpholine, we get compound **6** which can serve as a model fluorophore for **3**, **4** and particularly, **5**. Indeed, compounds **5** and **6** possess essentially identical electronic absorption spectra in basic solution (e.g. $\lambda_{\text{Abs,base}}$ values differ by only 3 nm). Lacking an amine side-chain, **6** naturally shows pH-independent photoproperties. It is most telling that **6** has a weak fluorescence ($\phi_{\text{Flu}} = 0.006$). The deactivation of the emissive ICT state due to twisted ICT state evolution is clearly displayed here.

Compounds **7** and **8** give us the opportunity to test electrostatic perturbations of the twisted ICT excited state from the opposite end of the π -electron system. Related studies in systems lacking twisting, e.g. **1** and its regioisomers, led to the control of PET rates by internal electric fields^{2,15} and by the presence of nodes in frontier orbitals.^{62,15} When the diethylamino- or morpholino-ethyl side-chains are protonated, the new cationic charge is again positioned two methylene groups away from the edge of the twisted ICT excited state. However, this edge carries only a fraction of the radical anionic charge spread over the naphthalimide frame. Thus the electrostatic effect, which should be a stabilization in this case, on the twisted ICT state is much smaller than those seen in **3** and **4**. Hence, the weak fluorescence is essentially pH-independent (Table 1) even though pK_a values can be coaxed from the emission spectra.

Compounds **5** and **6** can be mutated further into 6-amino-3H-benzimidazo[2,1-a]benz[d,e]isoquinolin-3-one derivatives **9** and **10** respectively by altering the imide functionality. Versions of these which are of the 'ICT fluorophore-spacer-receptor' type have been discussed previously.⁶³ Model fluorophore **10** has a weak and pH-independent fluorescence ($\phi_{\text{Flu,acid}} = 0.044$) which indicates the energy-sapping twisted ICT evolution at work. The latter originates from the pretwisting about the aromatic C- N bond near the morpholino unit. Piperazino-based **9** produces a H^+ -

induced fluorescence enhancement of 200-fold in a manner similar to that discussed for **5**.

Upto now, we have discussed structures which all contain a 1-aminonaphthalene core. Further structural space can be explored by proceeding to compounds **15** and **16**. Since the fluorescence switching behaviour of these and/or close relatives are available in the literature,^{5,7,27,64} it is sufficient to mention that these satisfy the classical PET system design of the ‘fluorophore-spacer-receptor’ model. Compounds **11-13** represent further movement along this mutational path. Naphthalene-1,8;4,5-diimides of this type have received much attention as electron deficient π -systems for catenane construction, whether by direct⁶⁵ or dynamic combinatorial⁶⁶ methods. Stacking of these fluorophores has also resulted in a sensing application.⁶⁷ Compound **11** is known and the quenching of its weak fluorescence by Fe^{3+} has been noted as well.⁵¹

Table 2. Various parameters for **11-13**, determined via pH-dependent uv-visible absorption and fluorescence spectroscopy.^a

Parameter	11	12	13
λ_{Abs}	343, 360, 381	342, 361, 382	342, 361, 382
$\log \epsilon^b$	4.10, 4.30, 4.40	4.12, 4.32, 4.44	4.08, 4.27, 4.36
λ_{Flu}^c	392, 413	394, 413	396, 413
$\phi_{\text{Flu,acid}}^d$	0.15	0.16	0.18
$\phi_{\text{Flu,base}}^d$	0.007	0.010	0.011
FE^e	21	16	17
pK_a^f	7.2	5.1	8.4

a. 10^{-5}M in methanol:water (1:4, v/v). Fluorescence emission spectra are obtained by excitation at λ_{Abs} . The subscripts ‘acid’ and ‘base’ in some of the parameters refer to the limiting value of a given parameter when the acid or base condition is increased respectively. The absorption spectral parameters are essentially pH-independent under our conditions.

b. ϵ in $\text{M}^{-1}\text{cm}^{-1}$.

c. Essentially pH-independent under our conditions.

d. uncertainty = 0.001 or 10% whichever is the larger.

e. H^+ -induced fluorescence enhancement factor = $\phi_{\text{Flu,acid}}/\phi_{\text{Flu,base}}$.

f. obtained by analyzing the pH dependence of the fluorescence intensity (I_{Flu}) or fluorescence quantum yield (ϕ_{Flu}) at a given wavelength according to the equation $\log[(\phi_{\text{Flu,acid}} - \phi_{\text{Flu}})/(\phi_{\text{Flu}} - \phi_{\text{Flu,base}})] = \text{pH} - \text{pK}_a$.⁵⁴ Uncertainty = 0.1.

Table 2 summarizes the results for compounds **11-13**. There is virtually no pH-dependence in all of the absorption and emission spectral parameters except for the fluorescence quantum yield, as is known for ideal fluorescent PET systems.⁴⁶ The pH-dependent fluorescence spectra for **11** are collected in Figure 2. Since the π -systems are rather symmetrical in **11-13**, there is no ICT character in the excited state so that no electrostatic perturbation is caused by the protonation of the receptor situated across the oligomethylene spacer. The H^+ -induced FE values are substantially large (ca. 20) in all three cases, in spite of the relatively electron-poor morpholine receptor within **12** and the rather long trimethylene spacer in **13**. A reason for this is the rather large driving force for PET in these systems owing to the electron deficiency of the fluorophore. In the instance of **11**, the application of the Weller equation⁶⁸ produces $\Delta G_{\text{PET}} = -1.8 \text{ eV}$. The calculation takes the excited state energy of the

naphthalenediimide to be 3.2 eV (calculated from the mean of the 0-0 band wavelengths in absorption and emission in Table 2), its reduction potential to be -0.70 V⁶⁵ and the oxidation potential of trimethylamine to be 0.76 V⁶⁹ (while ignoring solvent effects).

The classical physical organic chemistry interpretation⁷⁰ applies to the structural correlation of the pK_a values found for the various compounds. Thus, the more electron-rich diethylamino unit within **3** has a higher value (8.9) than that found for the dimethylamino unit within **4** (8.3). Closer positioning of the methylamino receptor within **5** or **9** to the electron-withdrawing 4-amino group owing to the piperazine ring produces the lowest pK_a value (7.3-7.4) observed in this study. The pK_a and pK_a' values are identical within experimental error in all available cases (Table 1) since the protonation occurs at a receptor which is external to the fluorophore where the excitation resides.⁷¹ The lowest pK_a' value (5.1 for compound **12**) found during this work arises for the morpholino unit containing the electron-withdrawing oxygen. Another contributor is the presence of the electron-withdrawing imide unit just two methylene groups away.

Summary and conclusions

We can conclude that steric preferences in the naphthalenic series can shift the mechanism of H⁺-induced fluorescence switching between PET and twisted ICT types. The PET mechanism requires an extra-fluorophoric amino receptor to deliver the electron, whereas the twisted ICT pathway relies on the twisting of an aromatic C-N bond within the fluorophore π -system. The extra-fluorophoric amino receptor serves as a cationically chargeable unit so that the twisted ICT excited state can be destabilized, thus weakening this deactivation channel. So we see that PET is directly influenced by amine protonation whereas twisted ICT pathway is controlled only via an electrostatic effect from some distance away. Unsurprisingly, PET designs are frequently found within sensing⁴²⁻⁴⁵ and logic⁷²⁻⁷⁶ systems. Careful attention to structural details will be required if twisted ICT mechanisms are to be similarly incorporated.

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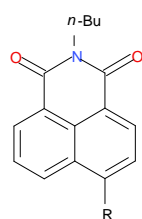
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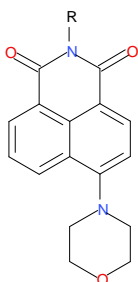
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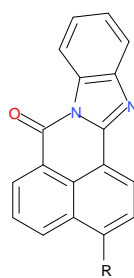
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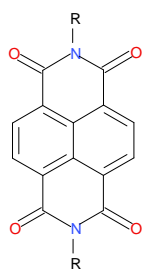
- 1; R = HNCH₂CH₂NEt₂
 2; R = Cl
 3; R = MeNCH₂CH₂NEt₂
 4; R = MeNCH₂CH₂NMe₂
 5; R = N(CH₂CH₂)₂NMe
 6; R = N(CH₂CH₂)₂O



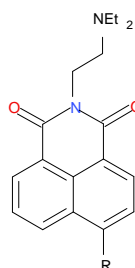
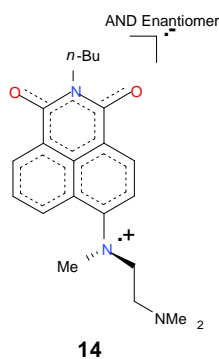
- 7; R = CH₂CH₂NEt₂
 8; R = CH₂CH₂N(CH₂CH₂)₂O



- 9; R = N(CH₂CH₂)₂NMe
 10; R = N(CH₂CH₂)₂O



- 11; R = CH₂CH₂NMe₂
 12; R = CH₂CH₂N(CH₂CH₂)₂O
 13; R = CH₂CH₂CH₂NMe₂



- 15; R = Cl
 16; R = H

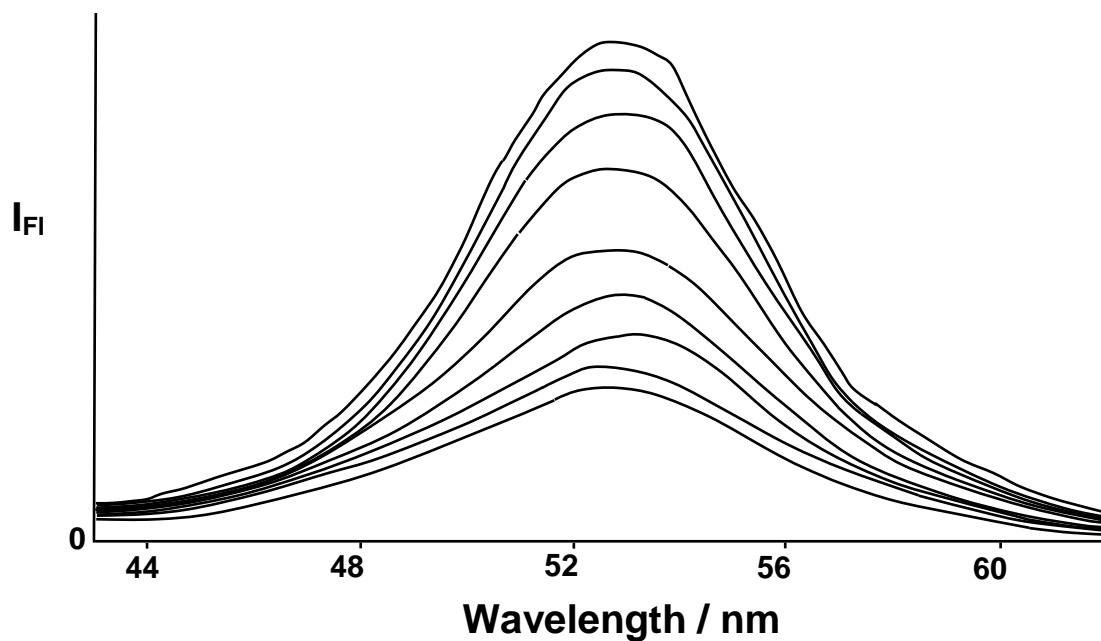


Figure 1. Fluorescence emission spectra of **4** as a function of pH. pH values in order of decreasing fluorescence intensity; 4.1, 5.1, 7.5, 7.9, 8.3, 8.7, 9.0, 9.3 and 9.7.

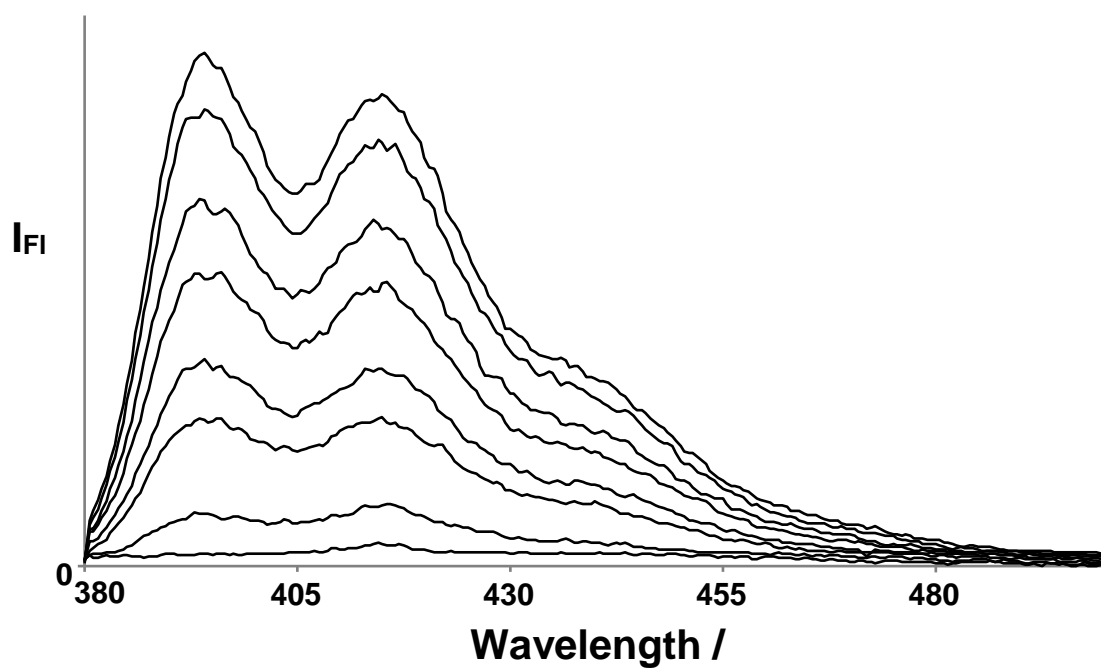


Figure 2. Fluorescence emission spectra of **11** as a function of pH. pH values in order of decreasing fluorescence intensity; 4.6, 6.1, 6.7, 7.0, 7.3, 7.5, 7.9 and 8.9.